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(21) International Application Number: PCT/US96/01261 (22) International Filing Date: 1 February 1996 (01.02.96) (30) Priority Data: 08/382,978 3 February 1995 (03.02.95) US (71) Applicant: SURPRENANT CABLE CORP. [US/US]; 172 Sterling Street, Clinton, MA 01510 (US). (72) Inventors: SHIEH, Tsu-chia; 9 Lomas Circle, Framingham, MA 01701 (US). NICOLL, William, A.; Apartment 22, 50 Commons Drive, Shrewsbury, MA 01545 (US). (74) Agent: SOLOWAY, Norman, P.; Hayes, Soloway, Hennessey, Grossman & Hage, 175 Canal Street, Manchester, NH 03101 (US).		(81) Designated States: European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: CROSSLINKED THERMOPLASTIC ELASTOMERS**(57) Abstract**

A crosslinked thermoplastic elastomer blend prepared by the process comprising blending together: (a) a thermoplastic resin containing at least three alternating blocks: A_x-B-A_x wherein A is a block of at least one polymerized unsaturated ethylene monomer of the following formula: $-CH_2-C(R_1)(R_2)-$, wherein R_1 and R_2 are each a hydrogen, alkyl or aromatic group, provided that when one of R_1 or R_2 is a hydrogen or an alkyl group, the other R group is an aromatic group; and wherein B is a block of a polymer or copolymer containing at least one conjugated diene monomer in polymerized form, having at least four (4) carbon atoms and the following formula for the residual double bond in the diene after polymerization: $-C(R_3)(R_4)-C(R_5)-C(R_6)-C(R_7)(R_8)-$, wherein $R_3 - R_8$ are each a hydrogen or an alkyl group, or mixtures thereof; (b) a thermoplastic polymer resin or mixture of thermoplastic resins; and (c) a crosslinking agent which develops crosslinking as between components (a) and (b) characterized in that the blend exhibits subsequent to crosslinking an elongation of less than 100 % under stress of 100 psi (6.8947 bar) at 200 °C.

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1 CROSSLINKED THERMOPLASTIC ELASTOMERS

2

3 The present invention relates to a crosslinked

4 thermoplastic elastomer blend composition superior in the

5 balance of rigidity, impact resistance and processability,

6 and in particular, resistance to elevated temperatures and

7 the ability to maintain a significant percentage of its

8 tensile strength, and elongation, upon exposure to heat.

9 In particular, the present invention is directed to the

10 preparation of a crosslinked thermoplastic elastomer blend

11 formulation which is suitable for use in either an

12 electrical insulating or tubing and hosing application,

13 and which displays unexpectedly high resistance to heat

14 aging and/or flame, good chemical resistance as well as

15 possessing highly satisfactory strength characteristics

16 over a broad temperature range.

17 There remains a continuous demand, especially in

18 the electronics industry, for thin-wall, truly low-cost

19 wire or cable insulation exhibiting high electrical

20 integrity and good physical properties. Towards this end,

21 two specific resins, poly(tetrafluorethylene) and

22 crosslinked polyethylene, have been popularized (along

23 with numerous others, e.g. fluorinated ethylene-propylene

24 resins and ethylene/tetrafluoroethylene copolymers) which

25 when used alone, or combined (i.e. layered) exhibit many

26 of the desired properties for an insulation application.

27 See, e.g. U.S. Patent No. 3,546,014.

28 That is, recognizing the virtues of both

29 polyethylene and fluorocarbon type polymers, electrical

30 insulation materials have been developed that combine both

31 a polyolefin and a fluoropolymer to prepare a composite

32 electrical insulating material with advantageous

33 performance. For example, in U.S. Patent No. 3,269,862,

34 it was reported that polyolefins such as polyethylene are

35 excellent insulating materials for electrical wires,

1 electric components and the like. However, the excellent
2 dielectric properties of polyolefins were said to be
3 offset by the relatively low melting points and their low
4 resistance to flame and oxidation. It was, therefore,
5 pointed out that considerable efforts had been directed to
6 developing polyolefin formulations which were not subject
7 to such deficiencies. Accordingly, the relatively low
8 melting point of polyethylene was reportedly improved by
9 crosslinking, e.g., by irradiation or chemical means. In
10 addition, it was further found that certain additives will
11 flame retard polyethylene. However, many flame retardant
12 additives adversely affect the dielectric properties of
13 polyolefins as well as low temperature performance and
14 corrosion resistance. The '862 disclosure went on to
15 report, therefore, a composite electrical insulating
16 material comprising a crosslinked polyolefin layer and a
17 crosslinked polyvinylidene fluoride layer which in
18 combination possessed a high degree of flame resistance
19 and a high degree of resistance to heat aging and high
20 strength characteristics over a broad temperature range.
21 The composite electrical insulating material disclosed
22 therein was found useful for insulating electrical wire
23 and electrical components with excellent dielectric
24 properties with respect to the coated wire substrate.

25 Building on the concept of a crosslinked polyolefin
26 base layer, followed by a fluoropolymer outer coating,
27 wherein the low melting point and low resistance to flame
28 and oxidation of the polyethylene layer is compensated by
29 crosslinking the polyethylene and coating with a
30 fluoropolymer, a variety of disclosures have been made for
31 producing materials suitable for insulation of wires and
32 electronic components and reference is made to the
33 following U.S. Patents: 3,763,222, 3,840,619, 3,894,118,
34 3,911,192, 3,970,770, 3,985,716, 3,995,091, 4,031,167,
35 4,155,823 and 4,353,961.

36 In addition, and of more recent report, is U.S. Patent

1 No. 5,281,766 which describes lead wire for use in motors,
2 coils and transformers, covered first with a layer of a
3 primary insulation material including a crosslinked
4 polyolefin followed by a second insulating jacket
5 comprising the specific fluoropolymer: poly(vinylidene
6 fluoride) or a poly(vinylidene fluoride) copolymer.

7 Accordingly, with the long-standing emphasis on a
8 fluoropolymer type insulation, the long-standing question
9 became whether or not such relatively expensive
10 fluoropolymer systems could be replaced by a different
11 thermoplastic resin composition which could be crosslinked
12 to a desired level, without sacrificing properties,
13 particularly the balance of tensile strength and
14 elongation, subsequent to standard heat aging requirements
15 for insulative materials. That being the case, a review
16 of the prior art was conducted to ascertain what types of
17 disclosures had been made with respect to crosslinked
18 thermoplastic resin compositions that might be suitable
19 for replacement of the previously described fluoropolymer
20 materials.

21 For example, in U.S. Patent No. 5,248,729, there is
22 described a thermoplastic resin composition prepared by
23 heat treating and crosslinking a mixture comprising (a) a
24 thermoplastic resin containing no olefinic unsaturation
25 and (b) an elastomer having an olefinic unsaturated
26 carbon-carbon bond, for example, styrene-butadiene-styrene
27 block copolymer. In particular, a dihydroaromatic
28 compound was used as the crosslinking agent in
29 crosslinking a mixture of a saturated thermoplastic resin
30 and an unsaturated elastomer. The crosslinking was said
31 to proceed only within the unsaturated component, with no
32 substantial change of the saturated thermoplastic resin.
33 The produced compositions were said to be superior in the
34 balance of rigidity, impact resistance and moldability.

35 In U.S. Patent No. 5,149,895, there is described a
36 vulcanizable liquid composition which comprises a styrene-

1 diene-styrene block copolymer, which is then crosslinked
2 to provide a vulcanizable composition. The polymers
3 produced were said to have high elongation and excellent
4 aging characteristics.

5 U.S. Patent No. 5,093,423 described a method for
6 making styrene-butadiene thermoplastic elastomers.
7 Specifically, the dynamic vulcanization of the styrene-
8 butadiene elastomer is reported, along with a co-
9 continuous matrix of styrene-ethylene-butadiene-styrene
10 block copolymer and polypropylene. The dynamic
11 vulcanization step is indicated to take place under
12 appropriate conditions of sheer and temperature.
13 Compositions of superior properties were reported to be
14 achieved using this particular method.

15 U.S. Patent No. 4,927,882 describes a styrene-
16 butadiene thermoplastic elastomer which is said to be
17 produced by dynamic vulcanization of the styrene-butadiene
18 component.

19 U.S. Patent No. 4,371,663 describes certain styrene
20 polymer/thermoplastic elastomer blends made by melt-
21 blending of styrene polymers and thermoplastic elastomers
22 followed by a heat initiated crosslinking reaction along
23 with the use of organic peroxides. Noteworthy
24 improvements in ESCR, tensile strength, and practical
25 toughness were said to be among significant physical
26 properties improved in such polyblends.

27 Finally, it should be noted that previous work known
28 to the present inventors related to blending together
29 styrene-ethylene-butylene-styrene block copolymers and
30 high and low density polyethylenes, in the presence of a
31 crosslinking agent, followed by crosslinking to low levels
32 of crosslink density. That is, these formulations
33 contained a crosslinking density below that of the present
34 invention and without the unexpected properties now
35 claimed.

36 In sum, therefore, all of the above formulations were

1 said to improve certain specific mechanical properties of
2 the resulting materials, but none reported on the
3 development of high levels crosslinking, or relative high
4 thermoset character, while at the same time maintaining
5 requisite flexibility for a wire coating, tubing or hosing
6 application. That is, none of the prior art formulations
7 described above report on material systems that can be
8 made thermoset to a desired degree, without sacrificing
9 the combined critical performance characteristics
10 necessary for an insulating material: high tensile
11 strength, sufficient flexibility and thermostability. In
12 short, the prior art has not been totally successful in
13 preparing a crosslinked thermoplastic elastomer suitable
14 to replace some of the more expensive materials used in
15 the insulated wire tubing or hosing industries.

16 Accordingly, it is an object of this invention to
17 provide a crosslinked thermoplastic elastomer which is
18 suitable for use as an insulating layer in the wire
19 coating industry and which is useful in other applications
20 where high tensile strength and flexibility are required,
21 such as cable jackets, tubing and hosing.

22 More particularly, it is an object of the present
23 invention to crosslink thermoplastic elastomer block
24 copolymers, wherein the crosslinking is carried out to a
25 level wherein flexibility is uniquely and surprisingly
26 preserved, high tensile strength is maintained, and
27 wherein both the tensile strength and flexibility remain
28 in the crosslinked resin subsequent to long-term thermal
29 aging.

30 Finally, it is a more specific object of the present
31 invention to develop a high tensile strength yet flexible
32 wire coating, tubing and hosing material stable to long
33 term heat aging suitable for wire insulating applications,
34 by the process of blending a thermoplastic elastomer block
35 copolymer with a thermoplastic polymer resin, and
36 crosslinking, wherein crosslinking is specifically

1 developed as between the thermoplastic elastomer and
2 thermoplastic polymer resin, at a desired level,
3 optionally in the presence of a crosslinking promoter,
4 along with incorporation of antioxidants and heat
5 stabilizers.

6 A crosslinked thermoplastic elastomer blend prepared
7 by the process comprising blending together:

8 (a) a thermoplastic resin containing at least three
9 alternating blocks:

10 $A_x-B_y-A_x$

11 wherein A is a block of at least one polymerized
12 unsaturated ethylene monomer of the following formula:

13 $-CH_2-C(R_1)(R_2)-$

14 wherein R_1 and R_2 are each a hydrogen, alkyl or aromatic
15 group, provided that when one of R_1 or R_2 is a hydrogen or
16 an alkyl group, the other R group is an aromatic group and
17 wherein B is a block of a polymer or copolymer containing
18 at least one conjugated diene monomer in polymerized form,
19 having at least four (4) carbon atoms and the following
20 formula for the residual double bond in the diene after
21 polymerization:

22 $-C(R_3)(R_4)-C(5)=C(R_6)-C(R_7)(R_8)-$

23 wherein R_3 - R_8 are each a hydrogen or an alkyl group, or
24 mixtures thereof; and

25 (b) a thermoplastic polymer resin or mixture of
26 thermoplastic resins;

27 (c) a crosslinking agent which develops crosslinking
28 as between components (a) and (b) characterized in that
29 the blend subsequent to crosslinking exhibits an
30 elongation of less than 100% under stress of 100 psi
31 (6.8947 bar) at 200°C.

32 The present invention comprises a variety of different
33 formulations which have been found, as noted above,
34 suitable for use in electrical insulation applications or
35 tubing or hosing applications, and which can be made
36 thermoset to a desired degree, to provide good tensile

1 strength, but which at the same time remain flexible, and
2 which can be made thermally stable. The details of these
3 formulations are described in the following embodiments.

4 In a first embodiment, the present invention can be
5 described as a crosslinked thermoplastic elastomer blend
6 prepared by the process comprising blending together:

7 (a) a thermoplastic resin containing at least three
8 alternating blocks:

9
$$A_x-B_y-A_x$$

10 wherein A is a block of at least one polymerized
11 unsaturated ethylene monomer of the following formula:

12
$$-CH_2-C(R_1)(R_2)-$$

13 wherein R_1 and R_2 are each a hydrogen, alkyl or aromatic
14 group, provided that when one of R_1 or R_2 is a hydrogen or
15 an alkyl group, the other R group is an aromatic group and
16 wherein B is a block of a polymer or copolymer containing
17 at least one conjugated diene monomer in polymerized form,
18 having at least four (4) carbon atoms and the following
19 formula for the residual double bond in the diene after
20 polymerization:

21
$$-C(R_3)(R_4)-C(5)=C(R_6)-C(R_7)(R_8)-$$

22 wherein R_3 - R_8 are each a hydrogen or an alkyl group, or
23 mixtures thereof; and

24 (b) a thermoplastic polymer resin or mixture of
25 thermoplastic resins;

26 (c) a crosslinking agent which develops crosslinking
27 as between components (a) and (b) characterized in that
28 the blend subsequent to crosslinking exhibits an
29 elongation of less than 100% under stress of 100 psi
30 (6.8947 bar) at 200°C (the details of this mechanical
31 behavior performance value is explained more fully in
32 connection with the working examples.) More preferably,
33 the blend exhibits an elongation of less than 90%, 80%,
34 70%, 60%, 50% or 40%, under stress of 100 psi (6.8947 bar)
35 at 200°C. In a most preferred embodiment the blend
36 exhibits an elongation of between 0-40%, again, under

1 stress of 100 psi (6.8947 bar) at 200°C.

2 In addition the above formulation can also have a 100%
3 Modulus value of less than 1600 psi (110.3152 bar) (again
4 the details of this mechanical behavior performance value
5 is explained more fully in connection with the working
6 examples), or values less than 1500 psi (103.4205 bar),
7 1400 psi (96.5258 bar), 1300 psi (89.6311 bar), and 1200
8 psi (82.7364 bar).

9 In a second embodiment, the present invention can be
10 described as a crosslinked thermoplastic elastomer blend
11 prepared by the process comprising blending together:

12 (a) a thermoplastic resin containing at least three
13 alternating blocks:

14 A_x-B-A_x

15 wherein A is a block of at least one polymerized
16 unsaturated ethylene monomer of the following formula:

17 $-CH_2-C(R_1)(R_2)-$

18 wherein R_1 and R_2 are each a hydrogen, alkyl or
19 aromatic group, provided that when one of R_1 or R_2 is a
20 hydrogen or an alkyl group, the other R group is an
21 aromatic group; and

22 wherein B is a block of a polymer or copolymer
23 containing at least one conjugated diene monomer in
24 polymerized form, having at least four (4) carbon atoms
25 and the following formula for the residual double bond in
26 the diene after polymerization:

27 $-C(R_3)(R_4)-C(R_5)=C(R_6)-C(R_7)(R_8)-$

28 wherein $R_3 - R_8$ are each a hydrogen or an alkyl group,
29 or mixtures thereof;

30 (b) a thermoplastic polymer or mixture of
31 thermoplastic polymers; and

32 (c) crosslinking components (a) and (b) upon exposure
33 to gamma ray, or electron beam irradiation, characterized
34 in that the blend exhibits an elongation of less than 100%
35 under stress of 100 psi (6.8947 bar) at 200°C. More
36 preferably, this blend formulation exhibits elongations of

1 less than 90%, 80%, 70%, 60%, 50% or 40% under stress of
2 100 psi (6.8947 bar) at 200°C. In a most preferred
3 embodiment the blend exhibits an elongation of between
4 0-40%, again, under stress of 100 psi (6.8947 bar) at
5 200°C.

6 In a third embodiment, the present invention can be
7 described as a crosslinked thermoplastic elastomer blend
8 prepared by the process comprising blending together:

9 (a) a thermoplastic resin containing at least
10 three alternating blocks:

11
$$A_x-B-A_x$$

12 wherein A is a block of at least one polymerized
13 unsaturated ethylene monomer of the following formula:

14
$$-CH_2-C(R_1)(R_2)-$$

15 wherein R_1 and R_2 are each a hydrogen, alkyl or
16 aromatic group, provided that when one of R_1 or R_2 is a
17 hydrogen or an alkyl group, the other R group is an
18 aromatic group; and

19 wherein B is a block of a polymer or copolymer
20 containing at least one conjugated diene monomer in
21 polymerized form, having at least four (4) carbon atoms
22 and the following formula for the residual double bond in
23 the diene after polymerization:

24
$$-C(R_3)(R_4)-C(R_5)=C(R_6)-C(R_7)(R_8)-$$

25 wherein $R_3 - R_8$ are each a hydrogen or an alkyl group,
26 or mixtures thereof;

27 (b) a thermoplastic polymer or mixture of
28 thermoplastic polymers; and

29 (c) crosslinking components (a) and (b) upon
30 exposure to gamma ray, or electron beam irradiation. This
31 formulation is characterized as having a 100% Modulus
32 value of less than 1600 psi (110.3152 bar), or values less
33 than 1500 psi (103.4205 bar), 1400 psi (96.5258 bar), 1300
34 psi (89.6311 bar), or 1200 psi (82.7364 bar).

35 In a still further embodiment, the present invention
36 can be described as a crosslinked thermoplastic elastomer
37 prepared by the process comprising

1 (a) supplying a thermoplastic resin containing at
2 least three alternating blocks:

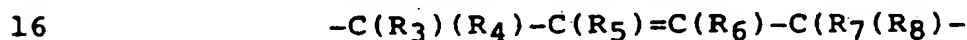


4 wherein A is a block of at least one polymerized
5 unsaturated ethylene monomer of the following formula:



7 wherein R_1 and R_2 are each a hydrogen, alkyl or
8 aromatic group, provided that when one of R_1 or R_2 is a
9 hydrogen or an alkyl group, the other R group is an
10 aromatic group; and

11 wherein B is a block of a polymer or copolymer
12 containing at least one conjugated diene monomer in
13 polymerized form, having at least four (4) carbon atoms
14 and the following formula for the residual double bond in
15 the diene after polymerization:



17 wherein $R_3 - R_8$ are each a hydrogen or an alkyl group,
18 or mixtures thereof; and

19 (b) crosslinking upon exposure to gamma ray, or
20 electron beam irradiation, characterized in that the
21 crosslinked elastomer exhibits an elongation of less than
22 100% under stress of 100 psi (6.8947 bar) at 200°C. More
23 preferably, the blend exhibits elongations of less than
24 90%, 80%, 70%, 60%, 50%, 40%, or 0-40%, under stress of
25 100 psi (6.8947 bar) at 200°C.

26 In still another embodiment, the present invention
27 comprises a crosslinked thermoplastic elastomer prepared
28 by the process comprising

29 (a) supplying a thermoplastic resin containing
30 at least three alternating blocks:



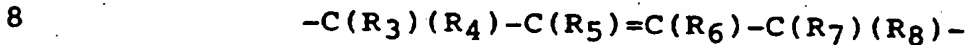
32 wherein A is a block of at least one polymerized
33 unsaturated ethylene monomer of the following formula:



35 wherein R_1 and R_2 are each a hydrogen, alkyl or
36 aromatic group, provided that when one of R_1 or R_2 is a

1 hydrogen or an alkyl group, the other R group is an
2 aromatic group; and

3 wherein B is a block of a polymer or copolymer
4 containing at least one conjugated diene monomer in
5 polymerized form, having at least four (4) carbon atoms
6 and the following formula for the residual double bond in
7 the diene after polymerization:



9 wherein $R_3 - R_8$ are each a hydrogen or an alkyl group,
10 or mixtures thereof;

11 (b) crosslinking components upon exposure to
12 gamma ray, or electron beam irradiation. In addition,
13 this formulation is characterized as having a 100% Modulus
14 value of less than 1600 psi (110.3152 bar), or values less
15 than 1500 psi (103.4205 bar), 1400 psi (96.5258 bar), 1300
16 psi (89.6311 bar) or 1200 psi (82.7364).

17 Finally, in another embodiment, the present invention
18 is a crosslinked thermoplastic elastomer prepared by the
19 process comprising blending together

20 (a) a thermoplastic elastomer resin containing at
21 least three alternating blocks:

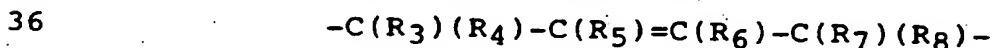


23 wherein A is a block containing at least one
24 polymerized unsaturated ethylene monomer of the following
25 formula:



27 wherein R_1 and R_2 are each a hydrogen, alkyl or aromatic
28 group, provided that when one of R_1 or R_2 is a hydrogen or
29 an alkyl group, the other R group is an aromatic group;
30 and

31 wherein B is a block of a polymer or copolymer
32 containing at least one conjugated diene monomer in
33 polymerized form, having at least four (4) carbon atoms
34 and the following formula for the residual double bond in
35 the diene after polymerization;



1 wherein R₃-R₈ are each a hydrogen or alkyl group, or
2 mixtures thereof;

3 (b) a crosslinking agent which develops
4 crosslinking in (a) characterized in that subsequent to
5 crosslinking the crosslinked elastomer exhibits an
6 elongation of less than 100% under stress of 100 psi
7 (6.8947 bar) at 200°C. More preferably, the blend
8 exhibits elongations of less than 90%, 80%, 70%, 60%, 50%,
9 40%, or 0-40%, under the stress of 100 psi (6.8947 bar) at
10 200°C.

11 In addition, the above embodiment can have a 100%
12 Modulus value of less than 1600 psi (110.3152 bar), or
13 values less than 1500 psi (103.4205 bar), 1400 psi
14 (96.5258 bar), 1300 psi (89.6311 bar), or 1200 psi
15 (82.7364 bar).

16 With respect to the above formulations, it has been
17 found that component (a) is preferably selected from the
18 group consisting of styrene-ethylene-butylene-styrene
19 copolymer, styrene-ethylene-butadiene copolymer, styrene-
20 butadiene-styrene copolymer, styrene-isoprene-styrene
21 copolymer, and mixtures thereof. The thermoplastic
22 component (b) is preferably selected from the group
23 consisting of polyethylene, poly(propylene), ethylene-
24 propylene copolymers, ethylene-propylene-diene terpolymer,
25 ethylene-octene copolymers, ethylene-butene copolymers,
26 ethylene-unsaturated carboxylate copolymers, polystyrene,
27 polyacrylonitrile, poly(alkyl alkylacrylate), polyamides,
28 polyesters, and mixtures thereof.

29 In addition, prior to crosslinking, the above
30 [Brmulations which recite the use of a crosslinking
31 component as component (c) preferably contain as the
32 component a crosslinking agent containing at least one
33 allyl or vinyl group, selected from the groups consisting
34 of esters of methacrylic acid, polyfunctional vinyl
35 monomers, and mixtures thereof. Preferably, the
36 crosslinking agent is triallyl isocyanurate,

1 triallylcyanurate, trimethylpropane trimethacrylate,
2 decamethylene glycol dimethacrylate, divinylbenzene,
3 diallylphthalate or mixtures thereof. Alternatively, the
4 crosslinking agent can be a compound which generates free
5 radicals upon exposure to heat, preferably of which is a
6 peroxide type compound.

7 The crosslinking agent is preferably present at a
8 concentration of at least one part of crosslinking agent
9 to 100 parts of resin components (a) and (b). More
10 preferably, the crosslinking agent is present at a
11 concentration of about 1-50 parts per 100 parts of resin
12 components (a) and (b), most preferably 10-20 parts. In
13 addition, all of the above crosslinking agents were found
14 to develop crosslinking as between components (a) and (b)
15 upon activation by heat, gamma ray or electron beam
16 irradiation. Finally, it is noted that crosslinking can
17 be developed upon exposure to moisture. Towards this end,
18 vinyl silane compounds can be utilized, in particular, a
19 vinyl triethoxy silane.

20 In connection with all of the above recited blends, it
21 has been found advantageous, depending upon the particular
22 application, to incorporate certain additives into the
23 inventive formulations.

24 In particular, it has been found advantageous to
25 incorporate heat stabilizers and antioxidants, either
26 alone or in combination. Preferred heat stabilizers are
27 those selected from the group of compounds known as the
28 zinc-mercapto heat stabilizers. Preferred antioxidants
29 are those selected from the group consisting of hindered
30 phenols, hindered aromatic amines, and mixtures thereof.

31 With respect to the above, it has been found that when
32 both an antioxidant and heat stabilizer are incorporated
33 into the various formulations, followed by crosslinking, a
34 thermal aging performance is achieved. Typically 7-8
35 parts of heat stabilizer, and 6-8 parts of antioxidant,
36 per 100 parts resin, are employed. That is, the amount of

1 additive is such that the crosslinked blends retain about
2 80% of their tensile strength after 7 days' exposure at
3 180°C.

4 In addition, flame retardants such as antimony or zinc
5 oxide, alone with halogen based flame retardants, such as
6 decabromodiphenyl oxide can be incorporated into the
7 blends. Moreover, metal deactivators can be readily
8 compounded in the formulations, e.g., hydrazide compounds.

9 With respect to the above crosslinked blends, the
10 degree of crosslinking is conveniently monitored by
11 measurement of certain physical properties, which is best
12 explained with reference to the following non-limiting
13 working examples.

14 Example I

15 A styrene-ethylene-butylene-styrene block copolymer
16 (KRATON G 1651) 50% by weight was combined (melt
17 compounding) with an ethylene-octene-copolymer (50% by
18 weight) along with TMPTMA. The amount of TMPTMA was about
19 15 parts per 100 parts by weight of the two aforementioned
20 copolymer resin components. Subsequent to irradiation
21 crosslinking of 25 megarads the blend formulation
22 indicated a tensile strength of about 2230 psi (153.7518
23 bar) and elongation of about 310%.

24 Example II

25 A styrene-ethylene-butylene-styrene block copolymer
26 (KRATON G 1651, 67% by weight) and an ethylene-propylene-
27 diene terpolymer (33% by weight) were combined with TMPTMA
28 (12 parts per 100 parts by weight of resin). Subsequent
29 to melt compounding the blend was crosslinked upon
30 exposure to 20 megarads irradiation.

31 Example III

32 A styrene-ethylene-butylene-styrene copolymer (KRATON
33 G 1651, 75% by weight) was combined with an ethylene-vinyl
34 acetate copolymer (25% by weight) along with TMPTMA (7
35 parts per 100 parts by weight of resin). Subsequent to
36 melt compounding the formulation was crosslinked by

1 radiation of 40 megarads.

2 Example IV

3 A styrene-ethylene-butylene-styrene block copolymer
4 (KRATON G 1651, 40% by weight) was blended with an
5 ethylene-octene copolymer (40% by weight) along with an
6 ethylene-vinyl acetate copolymer (20% by weight). This
7 resin combination was then combined with TMPTMA (15 parts
8 per 100 parts by weight of resin) and crosslinked by
9 irradiation of 20 megarads.

10 Example V

11 A styrene-ethylene-butylene-styrene block copolymer
12 (67% by weight) was combined with an ethylene-octene
13 copolymer (33% by weight) followed by the incorporation of
14 TMPTMA at 13 parts per 100 weight of resin subsequent to
15 melt compounding the blend was irradiation crosslinked
16 with 20 megarads.

17 Example VI

18 A styrene-ethylene-butylene-styrene copolymer was
19 mixed with TMPTMA at 20 parts per 100 parts by weight of
20 copolymer and crosslinked by irradiation of 7 megarads.

21 Example VII

22 A styrene-ethylene-butylene-styrene block copolymer
23 (67% by weight) was mixed with an ethylene-octene
24 copolymer (33% by weight) and TMPTMA (11 parts by weight
25 of resin). Subsequent to melt compounding the formulation
26 was irradiated with 20 megarads.

27 Example VIII

28 A styrene-ethylene-butylene-styrene block copolymer
29 (55% by weight, a polyethylene (35% by weight) and an EPDM
30 (10% by weight) were combined with TMPTMA (7.5 parts by
31 weight of resin). Subsequent to melt compounding the
32 blend was irradiation crosslinked with 15 megarads.

33 Example IX

34 A styrene-ethylene-butylene-styrene block copolymer
35 (67% by weight) was mixed with a polyethylene (33% by
36 weight) and TMPTMA (6 parts by weight of resin).

1 Subsequent to melt compounding the formulation was
2 irradiated with 20 megarads.

3 Example X

4 A styrene-ethylene-butylene-styrene block copolymer
5 (33% by weight) and an ethylene-octene copolymer (67% by
6 weight) were mixed with TMPTMA (12 parts by weight of
7 resin). Subsequent to melt compounding the blend was
8 irradiated with 20 megarads.

9 Properties of Blend Formulations

10 The above blend formulations were further mixed with
11 anti-oxidant and heat stabilizer compounds wherein the
12 amount of anti-oxidant and the amount of heat stabilizer
13 were both incorporated at a level of about 7% by weight.
14 The anti-oxidant was a hindered phenol compound,
15 specifically IRGANOX 1010, and the heat stabilizer was a
16 zinc mercapto compound. These particular additives were
17 combined in the melt compounding step. Subsequent to
18 irradiation crosslinking, all of these blends demonstrated
19 their ability to retain at least 80% of their original
20 tensile strength and elongation after seven days at 180°C
21 and showed no appreciable embrittlement after seven days
22 at 200°C in air. In addition, it was found that by
23 increasing the amount of TMPTMA and the irradiation dose,
24 the blend of Example II became very resistant to hot oil
25 (e.g. 150°C and ASTM No. 2 oil) and hot sharp chisel (e.g.
26 1 mil chisel with 500 gram weight at 250°C).

27 Hot Modulus and

28 100% Modulus at Room Temperature

29 A first convenient way to demonstrate the degree of
30 crosslinking of the above-referenced blends is to expose
31 the material to tensile stress at a temperature above its
32 melting point. In this invention, we subject test
33 specimens to 100 psi (6.8947 bar) stress at 200°C,
34 determine the resulting deformation and compute what is
35 referred to as the "Hot Modulus".

36 Specifically, a cut dumbbell or insulating tubing

1 whose cross section has been determined is annealed in
2 200°C oven for two minutes, removed, cooled to room
3 temperature and applied with bench marks of 1 inch. The
4 specimen suspended vertically in a 200°C oven is attached
5 a weight equivalent to 100 psi (6.8947 bar). The specimen
6 is allowed to remain in the oven for about 15 minutes.
7 The weighted specimen is then carefully removed from the
8 oven and allowed to cool to room temperature. The weight
9 is removed and the distance between the bench marks is
10 measured. Hot Modulus is defined as a percent of the
11 increase in distance between the bench marks over the
12 original 1 inch (2.54 cm) distance.

13 A convenient way of expressing flexibility of the
14 crosslinked thermoplastic elastomer blends is to measure
15 the stress required to elongate 100% of the material at
16 room temperature. This is referred to as the "100%
17 Modulus".

18 Specifically, a cut dumbbell or insulation tubing
19 whose cross section has been determined is applied with
20 bench marks of 1 inch (2.54 cm). The specimen is
21 subjected to a tensile and elongation test on a tensile
22 tester, such as Instron. The load that is required to
23 elongate the bench marks to 2 inches (5.08 cm) is
24 determined. 100% Modulus (psi) is defined by dividing the
25 load (pound) by the cross section (square inch) of the
26 specimen.

27 In the context of the present invention, wherein a
28 crosslinked thermoplastic material has been produced
29 having utility as wire/cable insulation, and as a resin
30 for a tubing or hose application, it has been found that
31 the Hot Modulus value is under 100%, preferably under 90%,
32 more preferably under 80%, and in a most preferred
33 embodiment under 70%. Alternatively, the resins of the
34 present invention can be characterized as having 100%
35 Modulus values of less than 1600 psi (110.3152 bar),
36 preferably under 1500 psi (103.4205 bar), more preferably

1 under 1400 psi (96.5258 bar), and in a most preferred
2 embodiment under 1200 psi (89.6311 bar).

3 In addition to the above, the following properties of
4 the blend formulations in the previously mentioned
5 examples were determined:

6 <u>Properties of Blend Formulation</u>				
7	Tensile		Hot Modulus	
8	Strength		(200°C/6.8947	
9	<u>Example</u>	<u>(bar)</u>	<u>bar) (%)</u>	<u>100% Modulus</u>
10				<u>(bar)</u>
11	I	153.7518	310	25.3
12	II	180.6411	270	25.0
13	III	120.6573	150	18.1
14	IV	166.8517	240	32.4
15	V	158.5781	250	34.8
16	VI	186.1569	290	24.2
17	VII	136.5151	230	42.6
18	VIII	153.7518	275	89.8
19	IX	155.1308	220	70.3
20	X	165.4728	330	57.2

21
22 As can be seen from the above, the crosslinked
23 thermoplastic blends of the present invention are
24 characterized in that the blends can exhibit an elongation
25 of less than 100% under a stress of 100 psi (6.8947 bar)
26 at 200°C. In addition, the blends can exhibit a 100%
27 modulus of less than 1600 psi (110.3152 bar) at room
28 temperature.

CLAIMS

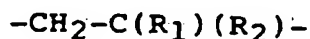
We claim:

1. A crosslinked thermoplastic elastomer blend prepared by the process comprising blending together:

(a) a thermoplastic elastomer resin containing at least three alternating blocks:

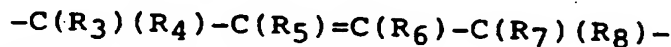
A-B-A

wherein A is a block containing at least one polymerized unsaturated ethylene monomer of the following formula:



wherein R_1 and R_2 are each a hydrogen, alkyl or aromatic group, provided that when one of R_1 or R_2 is a hydrogen or an alkyl group, the other R group is an aromatic group; and

wherein B is a block of a polymer or copolymer containing at least one conjugated diene monomer in polymerized form, having at least four (4) carbon atoms and the following formula for the residual double bond in the diene after polymerization;



wherein R_3 - R_8 are each a hydrogen or alkyl group, or mixtures thereof;

(b) a thermoplastic polymer resin or mixture of thermoplastic resins;

(c) a crosslinking agent which develops crosslinking as between components (a) and (b);

characterized in that the blend subsequent to crosslinking exhibits an elongation of less than 100% under stress of 100 psi (6.8947 bar) at 200°C.

2. The crosslinked thermoplastic elastomer blend of claim 1 wherein component (a) is selected from styrene-ethylene-butylene-styrene copolymer, styrene-ethylene-butadiene copolymer, styrene-butadiene-styrene copolymer, styrene-isoprene-styrene copolymer, and mixtures thereof.

3. The crosslinked thermoplastic elastomer blend of

1 claim 1 wherein component (b) is selected from
2 polyethylene, poly(propylene), ethylene-propylene
3 copolymers, ethylene-octene copolymers, ethylene-butene
4 copolymers, ethylene-unsaturated carboxylate copolymers,
5 polystyrene, polyacrylonitrile, poly(alkyl alkylacrylate),
6 polyamides, polyesters, and mixtures thereof.

7 4. The crosslinked thermoplastic elastomer blend of
8 claim 1 wherein the crosslinking agent contains at least
9 one allyl or vinyl group selected from esters of
10 methacrylic acid, polyfunctional vinyl monomers, and
11 mixtures thereof, preferably triallyl isocyanurate,
12 triallylcyanurate, trimethylpropane trimethacrylate,
13 decamethylene glycol dimethacrylate, divinylbenzene,
14 diallylphthalate or mixtures thereof.

15 5. The crosslinked thermoplastic elastomer blend of
16 claim 1 wherein the crosslinking agent is a compound which
17 generates free-radicals upon exposure to heat, preferably
18 a peroxide.

19 6. The crosslinked thermoplastic elastomer blend of
20 claim 4 wherein the crosslinking agent is present at a
21 concentration of at least 1 part of crosslinking agent per
22 100 parts of resin components (a) and (b), preferably
23 about 1-50 parts per 100 parts of resin components (a) and
24 (b).

25 7. The crosslinked thermoplastic elastomer blend of
26 claim 1 wherein the crosslinking agent which develops
27 crosslinking as between components (a) and (b) is
28 activated to crosslink said components by gamma ray,
29 electron beam irradiation, heat or moisture.

30 8. The crosslinked thermoplastic elastomer blend of
31 claim 1 wherein the crosslinking agent is a vinyl silane
32 compound, preferably vinyl triethoxy silane.

33 9. The crosslinked thermoplastic elastomer blend of
34 claim 1 further containing a heat stabilizer, preferably a
35 zinc-mercapto compound.

36 10. The crosslinked thermoplastic elastomer blend of

1 claim 1 further containing an antioxidant, preferably a
2 hindered phenol, hindered aromatic amine, and mixtures
3 thereof.

4 11. A crosslinked thermoplastic elastomer blend
5 prepared by the process comprising blending together:

6 (a) a thermoplastic resin containing at least
7 three alternating blocks:

8 A-B-A

9 wherein A is a block of at least one polymerized
10 unsaturated ethylene monomer of the following formula:

11 $-\text{CH}_2-\text{C}(\text{R}_1)(\text{R}_2)-$

12 wherein R_1 and R_2 are each a hydrogen, alkyl or
13 aromatic group, provided that when one of R_1 or R_2 is a
14 hydrogen or an alkyl group, the other R group is an
15 aromatic group; and

16 wherein B is a block of a polymer or copolymer
17 containing at least one conjugated diene monomer in
18 polymerized form, having at least four (4) carbon atoms
19 and the following formula for the residual double bond in
20 the diene after polymerization:

21 $-\text{C}(\text{R}_3)(\text{R}_4)-\text{C}(\text{R}_5)=\text{C}(\text{R}_6)-\text{C}(\text{R}_7)(\text{R}_8)-$

22 wherein $\text{R}_3 - \text{R}_8$ are each a hydrogen or an alkyl group,
23 or mixtures thereof;

24 (b) a thermoplastic polymer or mixture of
25 thermoplastic polymers; and

26 (c) crosslinking components (a) and (b) upon
27 exposure to gamma ray, or electron beam irradiation
28 characterized in that the crosslinked blend exhibits an
29 elongation of less than 100% under stress of 100 psi
30 (6.8947 bar) at 200°C.

31 12. The crosslinked thermoplastic elastomer blend of
32 claim 11 wherein component (a) is selected from styrene-
33 ethylene-butylene-styrene copolymer, styrene-ethylene-
34 butadiene copolymer, styrene-butadiene-styrene copolymer,
35 styrene-isoprene-styrene copolymer, and mixtures thereof.

36 13. The crosslinked thermoplastic elastomer blend of

1 claim 11 wherein component (b) is selected from
2 polyethylene, poly(propylene), ethylene-propylene
3 copolymers, ethylene-octene copolymers, ethylene-butene
4 copolymers, ethylene-unsaturated carboxylate copolymers,
5 polystyrene, polyacrylonitrile, poly(alkyl alkylacrylate),
6 polyamides, polyesters, and mixtures thereof.

7 14. The crosslinked thermoplastic elastomer blend of
8 claim 11, further containing a heat stabilizer, preferably
9 a zinc mercapto compound.

10 15. The crosslinked thermoplastic elastomer blend of
11 claim 11 further containing an antioxidant, preferably a
12 hindered phenol, a hindered aromatic amine, and mixtures
13 thereof.

14 16. A crosslinked thermoplastic elastomer blend
15 prepared by the process comprising blending together:

16 (a) a thermoplastic resin containing at least
17 three alternating blocks:

18 A-B-A

19 wherein A is a block of at least one polymerized
20 unsaturated ethylene monomer of the following formula:

21 $-\text{CH}_2-\text{C}(\text{R}_1)(\text{R}_2)-$

22 wherein R_1 and R_2 are each a hydrogen, alkyl or
23 aromatic group, provided that when one of R_1 or R_2 is a
24 hydrogen or an alkyl group, the other R group is an
25 aromatic group; and

26 wherein B is a block of a polymer or copolymer
27 containing at least one conjugated diene monomer in
28 polymerized form, having at least four (4) carbon atoms
29 and the following formula for the residual double bond in
30 the diene after polymerization:

31 $-\text{C}(\text{R}_3)(\text{R}_4)-\text{C}(\text{R}_5)=\text{C}(\text{R}_6)-\text{C}(\text{R}_7)(\text{R}_8)-$

32 wherein $\text{R}_3 - \text{R}_8$ are each a hydrogen or an alkyl group,
33 or mixtures thereof;

34 (b) a thermoplastic polymer or mixture of
35 thermoplastic polymers; and

36 (c) crosslinking components (a) and (b) upon

1 exposure to gamma ray, or electron beam irradiation.

2 17. A crosslinked thermoplastic elastomer prepared by
3 the process comprising blending together

4 (a) a thermoplastic elastomer resin containing at
5 least three alternating blocks:

6 A-B-A

7 wherein A is a block containing at least one
8 polymerized unsaturated ethylene monomer of the following
9 formula:

10 $-\text{CH}_2-\text{C}(\text{R}_1)(\text{R}_2)-$

11 wherein R_1 and R_2 are each a hydrogen, alkyl or aromatic
12 group, provided that when one of R_1 or R_2 is a hydrogen or
13 an alkyl group, the other R group is an aromatic group;
14 and

15 wherein B is a block of a polymer or copolymer
16 containing at least one conjugated diene monomer in
17 polymerized form, having at least four (4) carbon atoms
18 and the following formula for the residual double bond in
19 the diene after polymerization;

20 $-\text{C}(\text{R}_3)(\text{R}_4)-\text{C}(\text{R}_5)=\text{C}(\text{R}_6)-\text{C}(\text{R}_7)(\text{R}_8)-$

21 wherein R_3 - R_8 are each a hydrogen or alkyl group, or
22 mixtures thereof;

23 (b) a crosslinking agent which develops
24 crosslinking in (a) characterized in that subsequent to
25 crosslinking the crosslinked elastomer exhibits an
26 elongation of less than 100% under stress of 100 psi
27 (6.8947 bar) at 200°C.

28 18. The crosslinked thermoplastic elastomer of claim
29 17, wherein component (a) is selected from styrene-
30 ethylene-butylene-styrene copolymer, styrene-ethylene-
31 butadiene copolymer, styrene-butadiene-styrene copolymer,
32 styrene-isoprene-styrene copolymer, and mixtures thereof.

33 19. The crosslinked thermoplastic elastomer of claim
34 17, wherein the crosslinking agent contains at least one
35 allyl or vinyl group selected from esters of methacrylic
36 acid, polyfunctional vinyl monomers, and mixtures thereof,

1 preferably triallyl isocyanurate, triallylcyanurate,
2 trimethylpropane trimethacrylate, decamethylene glycol
3 dimethacrylate, divinylbenzene, diallylphthalate and
4 mixtures thereof.

5 20. The crosslinked thermoplastic elastomer of claim
6 17 wherein the crosslinking agent is a compound which
7 generates free-radicals upon exposure to heat, preferably
8 a peroxide.

9 21. The crosslinked thermoplastic elastomer of claim
10 17 wherein the crosslinking agent is present at a
11 concentration of at least 1 part of crosslinking agent per
12 100 parts of resin components (a) and (b), preferably
13 about 1-50 parts per 100 parts of resin components (a) and
14 (b).

15 22. The crosslinked thermoplastic elastomer of claim
16 17, wherein the crosslinking agent which develops
17 crosslinking is activated to crosslink by gamma ray,
18 electron beam irradiation, heat or moisture.

19 23. The crosslinked thermoplastic elastomer of claim
20 17, wherein the crosslinking agent is a vinyl silane
21 compound, preferably vinyl triethoxy silane.

22 24. The crosslinked thermoplastic elastomer of claim
23 17 further containing a heat stabilizer, preferably a zinc
24 mercapto compound.

25 25. The crosslinked thermoplastic elastomer of claim
26 17 further containing an antioxidant, preferably a
27 hindered phenol, a hindered aromatic amine, and mixtures
28 thereof.

29 26. A crosslinked thermoplastic elastomer prepared by
30 the process comprising

31 (a) supplying a thermoplastic resin containing at
32 least three alternating blocks:

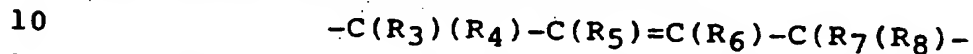
33 A-B-A

34 wherein A is a block of at least one polymerized
35 unsaturated ethylene monomer of the following formula:

36
$$-\text{CH}_2-\text{C}(\text{R}_1)(\text{R}_2)-$$

1 wherein R_1 and R_2 are each a hydrogen, alkyl or
2 aromatic group, provided that when one of R_1 or R_2 is a
3 hydrogen or an alkyl group, the other R group is an
4 aromatic group; and

5 wherein B is a block of a polymer or copolymer
6 containing at least one conjugated diene monomer in
7 polymerized form, having at least four (4) carbon atoms
8 and the following formula for the residual double bond in
9 the diene after polymerization:



11 wherein $R_3 - R_8$ are each a hydrogen or an alkyl group,
12 or mixtures thereof; and

13 (b) crosslinking upon exposure to gamma ray or
14 electron beam irradiation, characterized in that the
15 crosslinked elastomer exhibits an elongation of less than
16 100% under stress of 100 psi (6.8947 bar) at 200°C.

17 27. The crosslinked thermoplastic elastomer blend of
18 claim 26 wherein component (a) is selected from styrene-
19 ethylene-butylene-styrene copolymer, styrene-ethylene-
20 butadiene copolymer, styrene-butadiene-styrene copolymer,
21 styrene-isoprene-styrene copolymer, and mixtures thereof.

22 28. The crosslinked thermoplastic elastomer of claim
23 26, further containing a heat stabilizer, preferably a
24 zinc mercapto compound.

25 29. The crosslinked thermoplastic elastomer of claim
26 26, further containing an antioxidant, preferably a
27 hindered phenol, a hindered aromatic amine, and mixtures
28 thereof.

29 30. A crosslinked thermoplastic elastomer prepared by
30 the process comprising:

31 (a) supplying a thermoplastic resin containing
32 at least three alternating blocks:

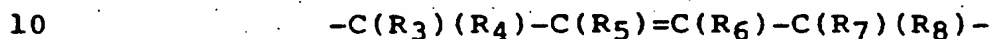
33
$$A-B-A$$

34 wherein A is a block of at least one polymerized
35 unsaturated ethylene monomer of the following formula:



1 wherein R_1 and R_2 are each a hydrogen, alkyl or
2 aromatic group, provided that when one of R_1 or R_2 is a
3 hydrogen or an alkyl group, the other R group is an
4 aromatic group; and

5 wherein B is a block of a polymer or copolymer
6 containing at least one conjugated diene monomer in
7 polymerized form, having at least four (4) carbon atoms
8 and the following formula for the residual double bond in
9 the diene after polymerization:



11 wherein $R_3 - R_8$ are each a hydrogen or an alkyl group,
12 or mixtures thereof;

13 (b) crosslinking components upon exposure to
14 gamma ray or electron beam irradiation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/01261

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 8/00, 291/02; C08L 53/00, 53/02

US CL : 525/92, 98, 193

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/92, 98, 193

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,159,016 (INOUE ET AL) 27 October 1992, columns 5 and 6.	1-30

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A document defining the general state of the art which is not considered to be of particular relevance	*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z document member of the same patent family
*O document referring to an oral disclosure, use, exhibition or other means	
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Date of the actual completion of the international search

26 MARCH 1996

Date of mailing of the international search report

09 APR 1996

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